rate of a'' is dominated by nonoptical contributions to the generalized oscillator strength. The LBH bands, for comparison, have no nonoptical contribution because the electronic transition is of the type $^1\Pi_g$–$^1\Sigma_g^+$. The a''–X (0–0) band is also favored by the Franck–Condon principle in electron-beam-excited spectra relative to emissions from low vibrational levels of $b\ ^1\Pi_u$ and $b'\ ^1\Sigma_u^+$ which would require vibrational de-excitation after Franck–Condon excitation from $v=0$ of $X\ ^1\Sigma_g^+$ such as is present in electric discharges at higher pressures, which indeed gives rise to strong emissions from the b and b' states.

Although an optical quadrupole f value of $\sim 10^{-7}$ is small compared to the f value associated with the LBH bands, it is not inconsistent with the results of the electron scattering experiments. It would be interesting, however, to observe the pure, sharp quadrupole lines at higher resolution either in absorption at pressures where broadening is negligible, or in emission so that accurate molecular constants of $N_2\ a''\ ^1\Sigma_g^+$ can be obtained. On the basis of the tentative assignments shown in Fig. 2, an approximate B_v' value of $B_0(a''\ ^1\Sigma_g^+) = 1.85 \pm 0.15$ cm^{-1} was obtained which can be compared to the expected "Rydberg value": $B_0(N_2^+\ X\ ^2\Sigma_g^+) = 1.92$ cm^{-1}.

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Ab Initio Calculations on the $H_2+D_2=2HD$ Four-Center Exchange Reaction. I. Elements of the Reaction Surface*

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We present the results of *ab initio* calculations on some interesting regions of the reaction surface for the four-center exchange reaction $H_2+D_2=2HD$. These calculations, which use a minimum basis set of Slater orbitals, indicate that for all geometries appropriate to the transition state of the reaction, a barrier height of at least 148 kcal/mole is present. This is far greater than the energy required to produce free radicals and more than three times the experimental energy of activation, 42 kcal/mole. Considering the sources and magnitudes for errors due to correlation and basis set restrictions, we estimate the barrier height for this exchange reaction to be 132 ± 20 kcal/mole exclusive of zero-point energies. In this paper we discuss the surface as determined by configuration interaction techniques. We find that the most favorable geometries for the exchange reactions are the square, rhombus, and kite configurations. However, all of these states are unstable with respect to H_2+2H. In addition we find no evidence of collision complexes for any of the likely transition state geometries. In the following paper we will examine the G1 wavefunctions for this system in order to obtain an understanding of the factors responsible for the shape of the surface.

INTRODUCTION

Bauer and Ossa[1] have recently found that the four-center exchange reaction

$$H_2+D_2=2HD$$

occurs in a shock tube between 1000° and 1400°K. Since this reaction is a prototype for a number of exchange reactions which are thought to occur by a four-center mechanism, it is of considerable interest to examine the reaction in detail from a theoretical point of view. We shall report herein an *ab initio* quantum-mechanical treatment of this reaction. We have found no transition state with a sufficiently low activation energy. In addition, none of the low-lying-transition states are metastable.

Calculations using a minimum basis set of Slater orbitals have been carried out by the configuration interaction (CI) and G1[2] methods. The familiar

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§ Contribution No. 3669.

[1] S. H. Bauer and E. Ossa, J. Chem. Phys, **45**, 434 (1966). This has been confirmed by A. Burcat and A. Lifshitz, *ibid.* **47**, 3079 (1967).

[2] W. A. Goddard III, Phys. Rev. **157**, 81 (1967).

Hartree–Fock (HF) method offers the advantage of an independent particle interpretation, but often behaves improperly upon dissociation because of the restriction to doubly occupied orbitals. The CI wavefunction behaves properly upon dissociation of the molecule; however, it does not lead to an independent particle model, and therefore sheds little light on the physics of the situation. The G1 wavefunction dissociates properly and retains an independent particle interpretation, and in particular, the G1 method leads to orbitals which show chemically reasonable behavior. Some geometries consistent with a four-center exchange mechanism were considered by these methods and all led to an energy above that of H_2+2H. In this article, we will discuss the reaction surface as obtained from CI calculations and compare this to the surfaces as obtained from some HF, and G1 calculations. In article II we will discuss the G1 results in detail and utilize the independent particle wavefunctions to better understand the shape of the surface encountered here.

The CI calculations presented here include all of the thirty-six possible configurations consistent with the Pauli principle which can be formed from four basis functions. All calculations use a minimum basis set of Slater orbitals, and all integrals have been evaluated without approximations by well-tested programs.[3]

In an exchange reaction, there exists a barrier along the reaction path. In the simplest case there is a single barrier and the transition state is a saddle point on the reaction surface. There is also the possibility that the transition state is metastable in which case there is a double barrier along the reaction path and a shallow well in between. Since the two species being exchanged are equivalent it is expected that the transition state will have a very high symmetry.

In the case of a highly symmetric configuration, e.g., the square configuration, the transition state may often be located by simply optimizing the scale, e.g., finding the square leading to the lowest energy. For the lower symmetry cases, the situation is more complicated, and we must search for a saddle point rather than a minimum. For a symmetric reaction such as two H_2 molecules reacting to give two other H_2 molecules, we would expect the reaction to be symmetric about the transition state. This requires equivalent sets of bonds in the transition state. There are very few symmetries which fulfill this condition, and most of them will be considered here, i.e., the square, rhombus, kite, centered equilateral triangle, and tetrahedron. In addition, we have considered certain other configurations, e.g., the regular trapezoid. (Most of the geometries considered in this work are graphically defined in Fig. 1.) We have also considered a number of distortions of each of these configurations.

We have studied the wavefunctions and energies of the low-lying states of the system as a function of the six independent geometric parameters. On the whole, we have concentrated our efforts on the region where we would expect to find a transition state, and special attention has been paid to the state to which two $^1\Sigma_g^+$ H_2 molecules at infinity would evolve in the course of an electronically adiabatic reaction.[4] (In all cases we neglect spin–orbit coupling, relativistic effects, and vibronic coupling.) Some of the reactions are discussed in terms of Aufbau diagrams[5] constructed in the Hartree–Fock approximation.[6]

For all nonplanar distortions examined, a restoring force toward the planar structure was found. This would seem to confirm the suggestion by Eyring that the transition state must be planar.[7] No transition

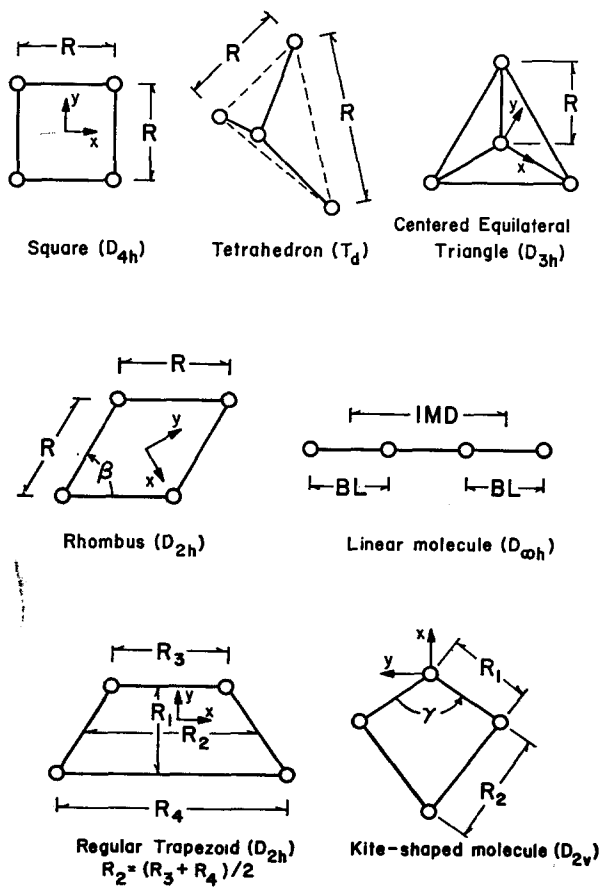


FIG. 1. Graphical definition of the nuclear configurations and geometrical parameters discussed in this work.

[3] All one- and two-electron integrals were carried out using zeta-function expansion programs developed at MIT and Harvard. We thank W. E. Palke and R. M. Pitzer for the use of these programs.

[4] This state is not necessarily either the ground state or the ground singlet state of the transition-state configuration.

[5] For the diatomic analog, see F. Hund, Z. Physik **63**, 719 (1930); and E. Wigner and E. E. Witmer, *ibid.* **51**, 859 (1928). This term has also been used by Herzberg [G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Co., Inc., Princeton, N.J., 1966), Vol. III, pp. 276f].

[6] The G1 results will be substantially similar if we consider the Hartree–Fock approximation as determining the symmetry of the two-electron orbitals. The aufbau principle for G1 wavefunctions becomes complex more in the general case.

[7] H. Eyring, J. Am. Chem. Soc. **53**, 2537 (1931).

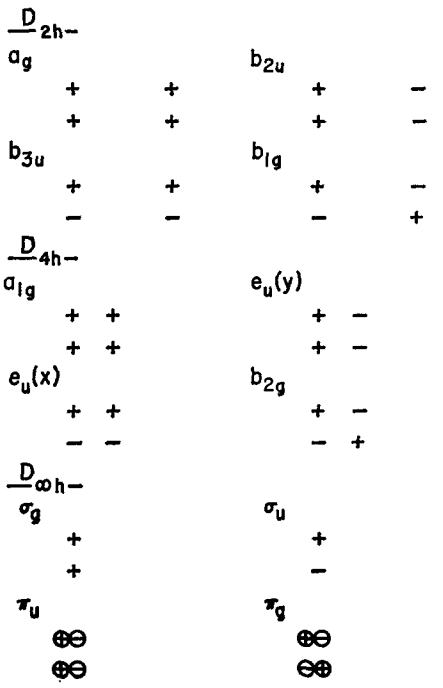


FIG. 2. The one-electron orbitals of rectangular H_2+H_2.

state with an energy below that of H_2+2H was found. The linear collision involved much lower energies; however, the linear configuration cannot be the transition state for the biomolecular exchange reaction.

Because we shall discuss only the electronic wavefunctions in the majority of the remainder of this work, isotopic differentiation will be suppressed.

THE TRANSITION STATES

Consider two H_2 molecules at infinite separation; each is totally independent of the other and the electrons occupy pure H_2 molecular orbitals, $1\sigma_g$, $1\sigma_u$, $\cdots$.[8] When the distance becomes finite, all the electrons must be considered together in a single system since they are indistinguishable. Even at large distances the one-electron states are dependent upon the relative orientation of the two molecules. For the purposes of this discussion, we shall define the unit of two H atoms which existed together at infinity as a *molecule* to distinguish this structure from the unit of four H atoms which we shall define as a *system*. In the center-of-mass system, this orientation will usually be specified by the following six independent position variables: R, the distance between the centers of the molecules, which we will call the intermolecular distance (IMD); θ, the angle between the planes specified by the two nuclei of one molecule and the center of the other; ϕ_1 and ϕ_2, the angle between the intercenter line and the internuclear bond line of molecules 1 and 2, respectively; and r_1 and r_2, the internuclear distances of each of the two molecules which we shall refer to as the bond lengths (BL).

[8] This applies only to the Hartree–Fock approximation.

We shall fix θ, ϕ_1, and ϕ_2 for the approach as those of the transition state in order to find the states which two H_2 molecules in $^1\Sigma_g^+$ states would evolve to. Calculations of these states as a function of geometry show that none has a sufficiently low energy to explain the experimental results.[1] We will see later that none of the configurations studied formed a metastable transition state, and that each is allowed to dissociate toward H_2+2H. These configurations require an activation energy much above the experimental energy of the free radical process ($H_2+D\cdot=HD+H\cdot$), 58 kcal.[9]

The Square Configuration

We shall consider the square as the transition state of a rectangular system; thus we have $\theta=0$, $\phi_1=\phi_2=\pi/2$, and $r_1=r_2$. Later we will consider it as formed from the rhombus. It can also be reached through nonplanar approaches, which we will not consider here.

In Fig. 2 we have graphically defined the orbitals of the system as it evolves. Originally, it has rectangular, D_{2h}, symmetry. At the transition state, it becomes square, D_{4h}; then it returns to rectangular symmetry. In Fig. 3, we illustrate the behavior of these levels. For the square, the second and third orbitals of the rectangle become degenerate. In this neighborhood, these two will be essentially degenerate, and configuration interaction will be an important factor. Further shortening of the intermolecular distance,[10] restores the rectangular symmetry with these two levels inverted.

When the intermolecular distance is decreased to zero, we generally reach a point of known ordering. We shall refer to this point as the united molecule limit by analogy with the Hund treatment[5] of the diatomic case. This point need not have physical significance for the reaction, but with a number of geometries, the compression to it is a realistic path over the surface. In the case under consideration, the rectangle, the united molecule limit is the He_2 molecule, which is not actually meaningful in the reaction.

Figure 3 may be viewed as an Aufbau diagram for the section of the reaction surface which is shown in Fig. 4. In the figures we have adopted the convention that T denotes its transition state, U denotes its united molecule limit, and ∞ denotes its separated molecule limit.

We will be concerned here only with the reaction of the molecules originally in their electronic ground states. Therefore, we place two electrons in the first level, two in the second level of the system at infinite separation,[11] and follow their behavior as the system is

[9] See for example A. Farkas and L. Farkas, Proc. Roy. Soc. (London) **A152**, 124 (1935). S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co., New York, 1941), p. 151.

[10] The term intermolecular distance and, indeed, the word molecule itself have lost their conventional meaning long before this. They have meaning only as defined above.

[11] For pedagogical convenience we are using orbital correlation diagrams in the usual inconsistent manner which neglects the incorrect dissociations of Hartree–Fock wavefunctions. Thus at large distances we really have in mind a GI, UHF, or limited CI wavefunction.

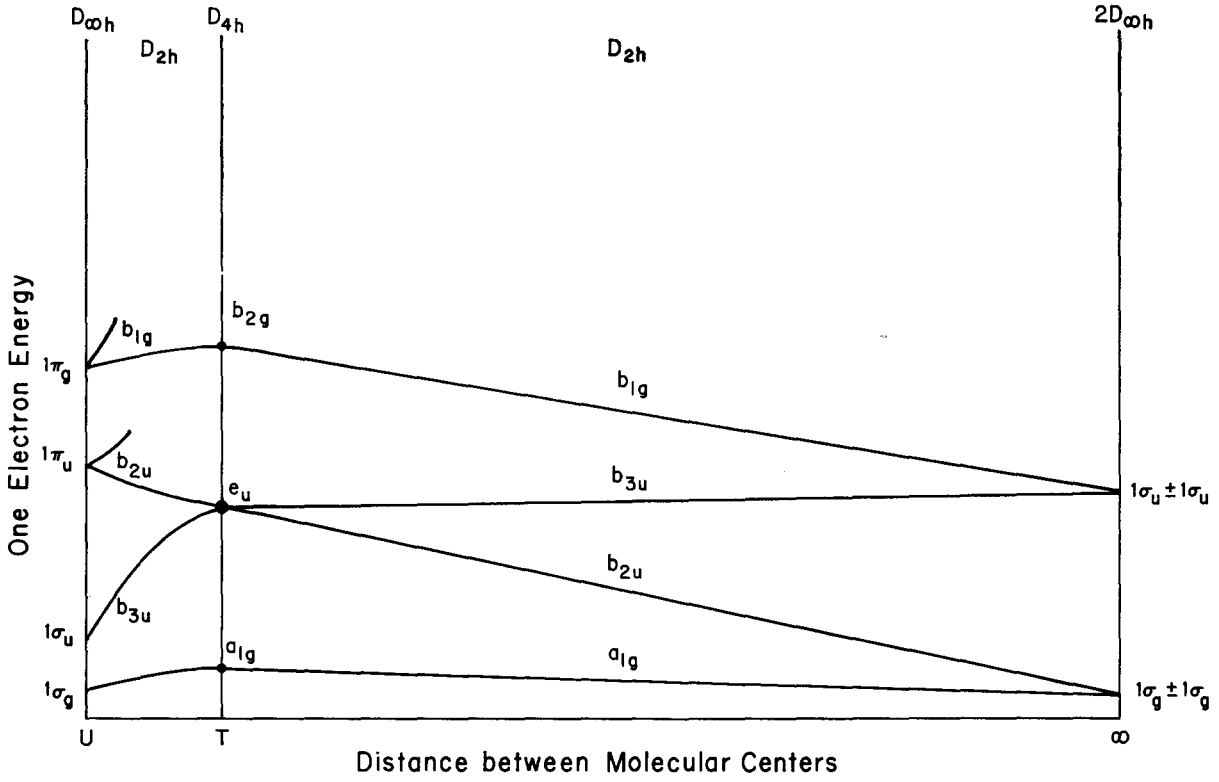


FIG. 3. The qualitative one-electron energy level scheme for rectangular H_2+H_2. T=square, $U=He_2$

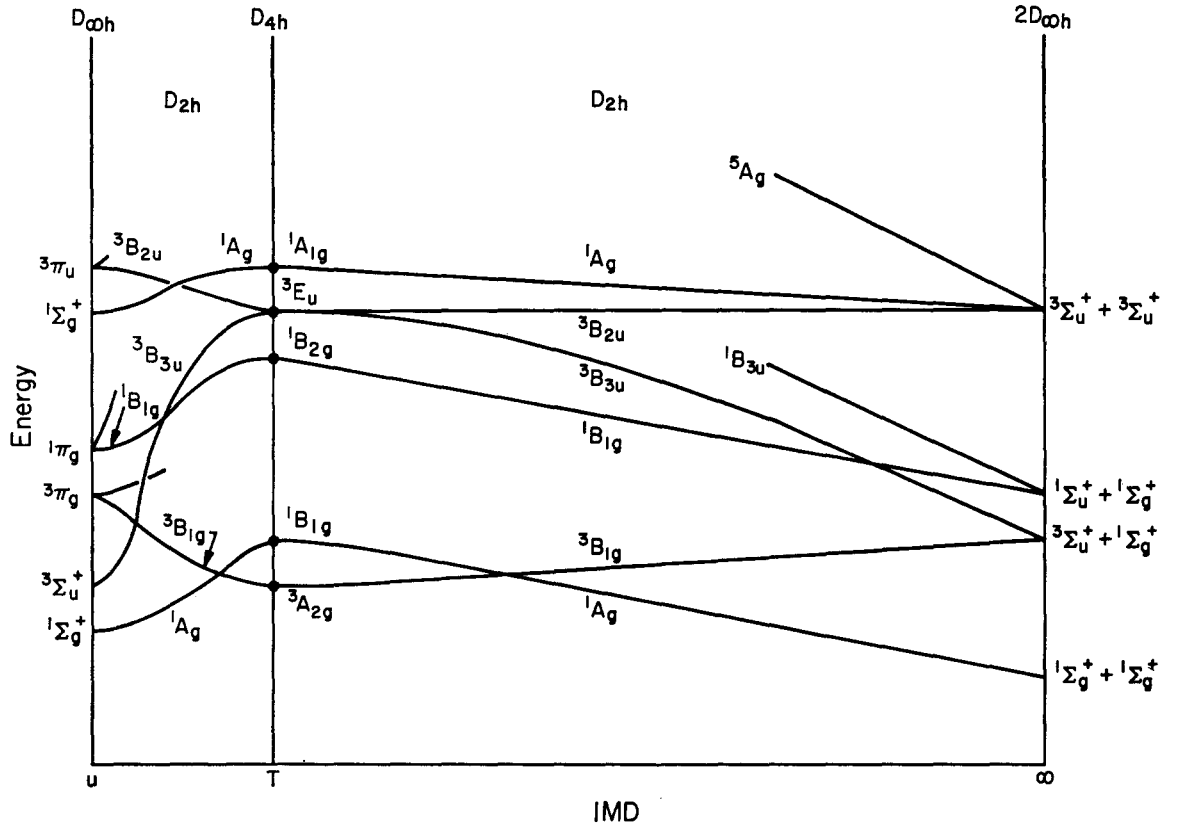
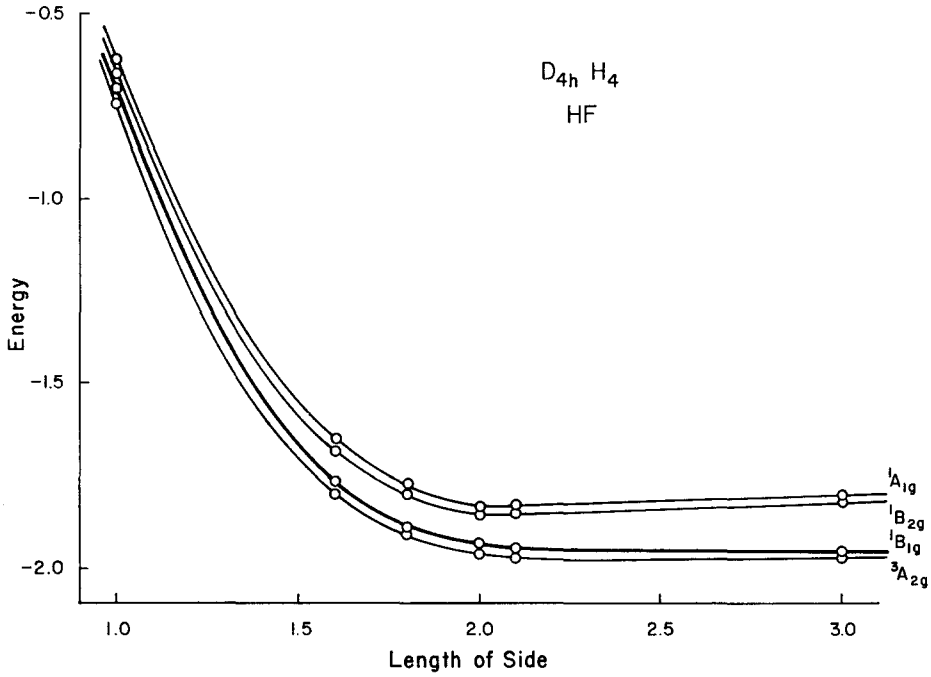
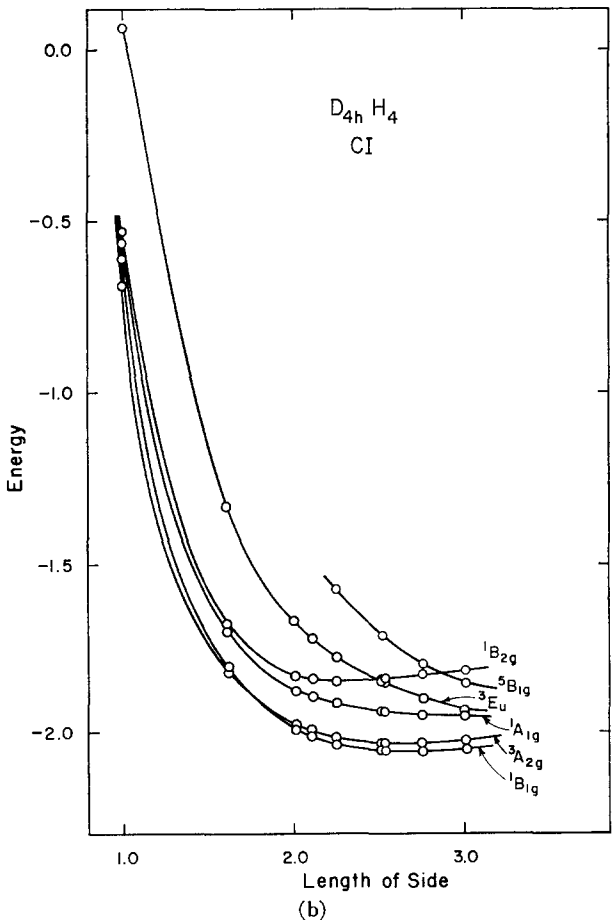


FIG. 4. The many-electron states of rectangular H_2+H_2.



(a)



(b)

FIG. 5. (a) The Hartree–Fock energy (in hartrees) of the first four states of D_{4h} (square) H_4 as a function length of side (in bohrs). (b) The CI energy (in hartrees) of the first six states of D_{4h} (square) H_4 as a function of distance.

TABLE I. The Hartree–Fock energies[a] (in hartrees[b]) for square H_4,[c] R is the length of the sides (in bohrs).

R (bohr)	$E(^3A_{2g})$ $a^2(xy-yx)$	$E(^1B_{1g})$ $a^2(x^2-y^2)$	$E(^1B_{2g})$ $a^2(xy+yx)$	$E(^1A_{1g})$ $a^2(x^2+y^2)$
1.0[d]	−0.758569	−0.712803	−0.666419	−0.620654
1.6[d]	−1.798114	−1.767358	−1.685533	−1.654767
1.8[e]	−1.903628	−1.877572	−1.781374	−1.754919
2.0[e]	−1.954525	−1.932052	−1.852233	−1.836574
2.1[e]	−1.969112	−1.948372	−1.844406	−1.823007
3.0[f]	−1.953094	−1.943146	−1.808935	−1.798987

[a] References 12 and 13.
[b] Reference 17.
[c] The HF energy of two H_2 for an optimized minimum basis set is −2.25638 hartrees at $R=1.4$.
[d] Orbital exponent = 1.05.
[e] Optimum orbital exponents used for each state.
[f] Orbital exponent = 1.00.

compressed. Thus, if we let the y axis lie along the IMD, the a_{1g} and b_{2u} levels are doubly occupied. At the transition state, the b_{2u} and b_{3u} levels of the D_{2h} system merge into the doubly degenerate e_u level of D_{4h} H_4. Two electrons in e_u states yield four nondegenerate many-electron states. Of these it is the $^1B_{1g}$ state of D_{4h} H_4 to which two ground-state molecules evolve. The qualitative behavior of the many-electron states of the system, from infinite separation to the united molecule limit, is presented in Fig. 4.

We present the Hartree–Fock[12,13] energies of the first four states of square H_4 in Fig. 5(a) and Table I. Full CI energies[14] of these states are presented in Fig. 5(b) and Table II. A crossing of the $^3A_{2g}$ [15] and $^1B_{1g}$ levels occurs at approximately $R=1.7$.[16,17] The $^1B_{1g}$ state exhibits a minimum of approximately $E=-2.06$ near $R=2.6$ while the energy for the separated molecules is −2.296. If this were the transition state for the exchange reaction, the barrier would be 148 kcal/mole which is about three times the experimental activation energy. We will see below that this state is unstable with respect to dissociation through a kite-shaped configuration into H_2+2H; thus this state could not be a metastable transition state.[18] Note that the HF calculations lead to $^1A_{1g}$ above $^1B_{2g}$, whereas the CI calculations show $^1B_{2g}$ to be above $^1A_{1g}$ for all R considered and above ^3E_u for $R>2.5$.

The Tetrahedral Configuration

Eyring[7] suggested that nuclear–nuclear repulsion was the dominant factor in the determination of the geometry of the transition state. Based on this assumption, he found that the transition state of this four-center exchange reaction could not be tetrahedral. In the following, we will present evidence based on *ab initio* quantum-mechanical calculations that his conclusion was right.

Consider our system again with large intermolecular distance. Let $\theta=\phi_1=\phi_2=\pi/2$, i.e., the two molecules are in perpendicular planes each bisected by the plane of the other. The two molecules are further required to be of equal length and perpendicular to the line formed by the intersection of these planes. Here the system has D_{2d} symmetry.

Figure 6 defines the one-electron orbitals, where we have chosen the intermolecular line to lie along the z axis. The qualitative behavior of the one-electron energy levels is illustrated in Fig. 7. As the intermolecular distance is decreased, we obtain a transition

[12] The wavefunctions use the proper linear combinations of two determinental wavefunctions to properly describe the symmetry of the square.
[13] Unless otherwise specified, all calculations presented in this paper use a minimum basis set (MBS) of 1s Slater orbitals with an orbital exponent of 1.05. For internuclear distances of 2.5 this value is near the optimum for several configurations for the various methods; thus for such configurations it is comparable to an optimized MBS calculation on a separate H_2 molecule.
[14] The valence bond configuration interaction work of V. Magnasco and G. F. Musso, J. Chem. Phys. **47**, 1723 (1967) includes a square of side 1.4166 bohr using an orbital exponent of 1.193. They report an energy of −1.67198 hartree; we find this structure to have an energy of −1.67180 hartree. This difference was traced to an incorrect value for their integral AD, BC (see Table VI of the above reference). They get 0.143378 whereas we obtain 0.143454 using a zeta-function expansion program (R. M. Pitzer, J. P. Wright, and M. P. Barnett, QCPE #24) and 0.143452 with a Gaussian transform program [I. Shavitt, *Methods of Computational Physics* (Academic Press Inc., New York, 1963), Vol. II, p. 1]. *Note added in proof:* V. Magnasco and G. F. Musso [J. Chem. Phys. **50**, 571 (1969)] have confirmed this error.
[15] Note that this is the state which Griffing and Mǎcek [J. Chem. Phys. **23**, 1029 (1955)] have labeled $^3B_2$.
[16] Griffing and Mǎcek (Ref. 15) find an ordering consistent with our Hartree–Fock results but inconsistent with these CI results.
[17] Atomic units are used throughout, in these units $e=\hbar=m_e=1$; 1 hartree = 27.211 eV = 627.51 kcal/mole is the unit of energy and 1 bohr = 0.52917 Å is the unit of length. [E. R. Cohen, J. W. M. Du Mond, Rev. Mod. Phys. **37**- 537 (1965)].
[18] We find that the lowest state of the square will not distort into the rhombus, this would seem to be inconsistent with the results of K. Morokuma, L. Pedersen, and M. Karplus, J. Am. Chem. Soc. **89**, 5064 (1967). However, their results are consistent with ours (see Fig. 14); they find the ^1A_g and $^1B_{1g}$ states of the rhombus to cross at 62° for a rhombus of side 2.5 bohr (M. Karplus, private communication).

TABLE II. CI energies[a] (in hartrees)[b] of square H_4.[c] The length of a side is R (in bohrs).

R	$E(^3A_{2g})$	$E(^1B_{1g})$	$E(^1A_{1g})$	$E(^1B_{2g})$
1.0	−0.770184	−0.741294	−0.667230	−0.648307
1.6	−1.821210	−1.816794	−1.703317	−1.687097
2.0	−1.988642	−1.997470	−1.877013	−1.831324
2.1	−2.007114	−2.018721	−1.897805	−1.843529
2.25	−2.024798	−2.040106	−1.919766	−1.851389
2.5	−2.036498	−2.056603	−1.940981	−1.845425
2.54	−2.036984	−2.057685	−1.943278	−1.842923
2.75	−2.035710	−2.058721	−1.952708	−1.825155
3.0[d]	−2.032207	−2.053970	−1.965413	−1.817671

[a] References 4 and 7.
[b] Reference 17.
[c] The CI energy of two H_2 for an optimized minimum basis set is −2.29587 hartree at $R=1.4304$. This is the appropriate separated molecule limit for CI, G1, and GF.
[d] Orbital exponents = 1.00.

state with T_d symmetry. The triple degeneracy of the second one-electron level leads to four many-electron states. Further shortening of the intermolecular distance restores the D_{2d} symmetry with an inversion of the e and b_2 levels. The united molecule limit is the square structure discussed above.

Figure 8 shows that the set of states arising in this geometry is somewhat complicated. Two $^1\Sigma_g^+$ H_2 molecules go into the ^1E state of the transition state. Figure 9 and Table III show the CI energy of the first four states of this geometry in the range of reasonable internuclear distances; the magnitude of the energy rules out this configuration as a possible transition state for the exchange reaction.

The Centered Equilateral Triangular Configuration

Let us again consider the system with a large internuclear distance. Let $\theta=\phi_1=0$ and $\phi_2=\pi/2$, i.e., the system now consists of two coplanar molecules. One molecule lies along the intermolecular line while the other is perpendicular to it, and r_1 is allowed to be different from r_2. The system possesses C_{2v} symmetry until it reaches the D_{3h} [19] transition state (here $r_2=\sqrt{3}r_1$). Further compression reestablishes the C_{2v} symmetry (the kite-shaped geometry discussed below) and eventually reaches the united molecule limit, a rhombus. In the figures, we have chosen the square as this limit.

The qualitative behavior of the orbital energies for the one-electron levels is shown in Fig. 10. At the transition state the second one-electron level is an e orbital, and therefore we have an open-shell system. In Fig. 11 we illustrate the behavior of the many-electron states; two $^1\Sigma_g^+$ H_2 molecules go into the E' state. The HF, G1, and CI energies for this state are given in Fig. 12 and Table IV.

The transition state for this symmetry can be determined by optimizing a scaling factor. When the shortest distances in the system are near 2.5 bohr, the system is stable with respect to four atoms, but quite unstable with respect to H_2+2H. The system could not exist as a metastable species because there are two unobstructed routes to the kite which could then dissociate toward linear H_3 and H. The first is the path from the equilateral triangle to the united molecule limit described above. The second which exhibits a somewhat higher force is the twisting of the shorter molecule into the kite-shaped configuration.

In Fig. 13 and Table V, we give the G1 and CI energies for a path corresponding to the first mechanism. Here we have restricted the three shortest distances in the D_{3h} configuration to remain fixed at 2.2 bohr, the angular parameter is the largest interior angle between these three lines; for the equilateral triangle, it is 120°,

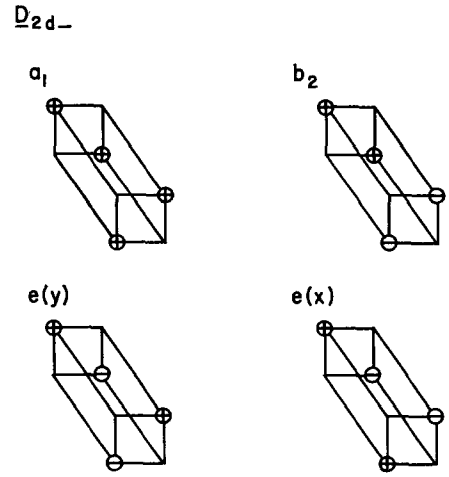


FIG. 6. The one-electron orbitals of staggered (D_{2d}) H_2+H_2.

[19] In order for an exchange reaction to occur here, the system must attain a geometry in the region of the centered-equilateral triangle. The choice of exactly D_{3h} over some nearby configuration is a matter of computational convenience. The choice of the united molecule limit here was made in a similar spirit.

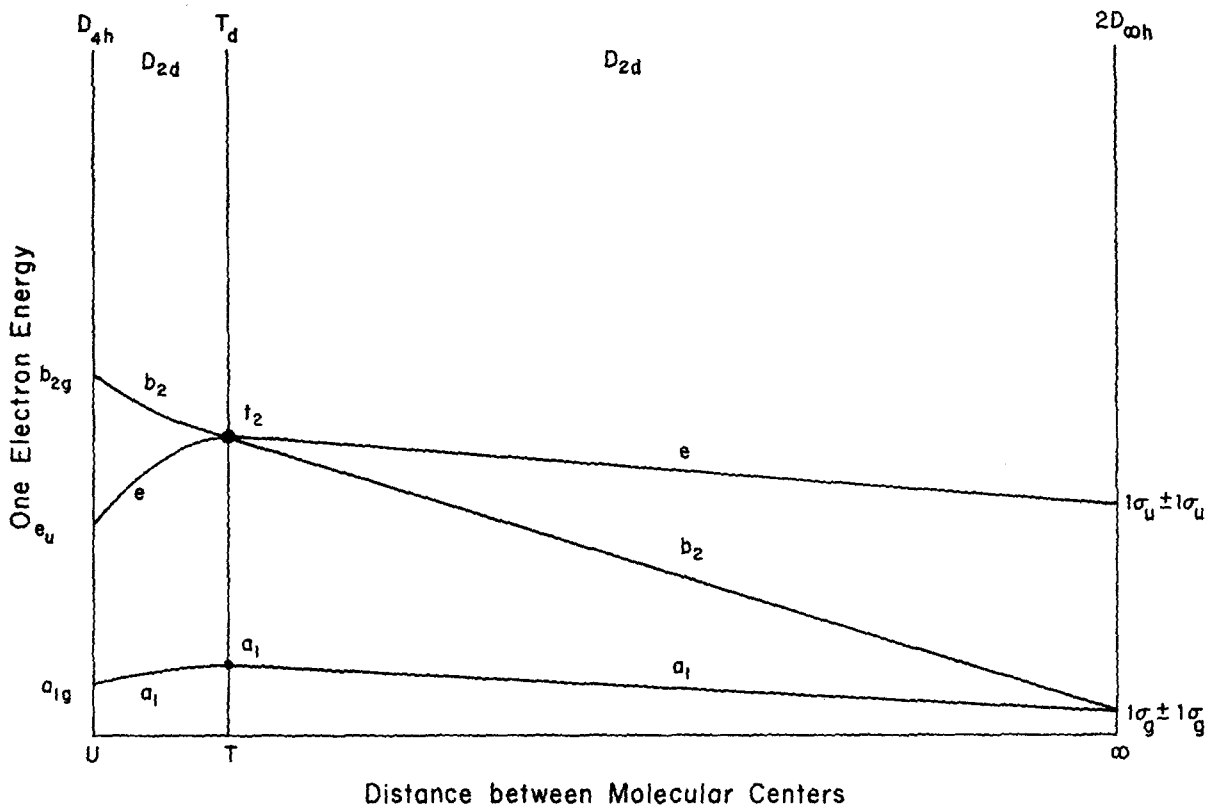


FIG. 7. The qualitative one-electron energy level scheme for staggered (D_{2d}) H_2+H_2.

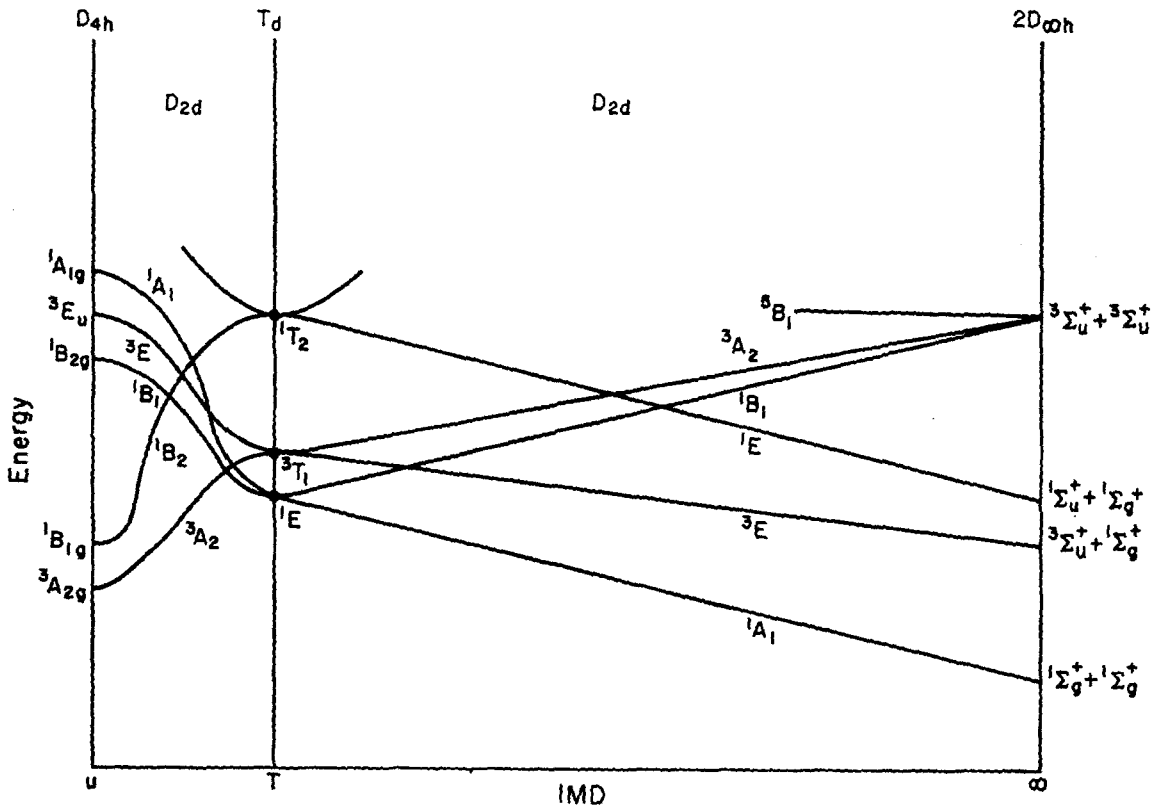


FIG. 8. The many-electron states of staggered (D_{2d}) H_2+H_2.

TABLE III. The CI energies[a] (in hartrees)[b] for tetrahedral H_4.

R	$E(^1E)$	$E(^3T_1)$	$E(^1T_2)$	$E(^1A_1)$
2.0	−1.758028	−1.747276	−1.553564	−1.458255
2.2	−1.839236	−1.824235	−1.617258	−1.520086
2.4	−1.894076	−1.876088	−1.655718	−1.556894

[a] Reference 13. [b] Reference 17.

for a 60° rhombus, 240°. The minimum occurs at 210°, a kite-shaped configuration.

The Rhombic Configuration

Once again, consider the system at large intermolecular separation, but this time, let $\theta=0$ and $\phi_1+\phi_2=\pi$, i.e., parallel, coplanar molecules. This rhomboidal (or rectangular) system proceeds to a rhombic transition state, and into a linear H_4 (or He_2) united molecule limit, respectively. The definitions of the one-electron states and the Aufbau diagrams are similar to those of the square (of course, the square is just a special rhombus). These orbitals and their qualitative behavior are shown in Figs. 2 and 3, where degeneracy of the e_u level is lifted for $\phi_1\neq\pi/2$. Thus we are dealing with a closed-shell system, but there is a near degeneracy for angles near 90 deg. The many-electron energy rises upon rhomboidization of the rectangle, (i.e., slightly displacing one H_2 parallel to the axis of the other H_2, resulting in a rhomboid).

In order to determine whether any states of the square might be more stable for the rhombus distortion, we carried out calculations for a number of states as a function of the interior angle of the rhombus (with a fixed side of 2.54 bohr), as shown in Fig. 14 and Table VI. We found that the two lowest states of the square, $^1B_{1g}$ and $^3A_{2g}$, are stable with respect to rhombic distortion,[18] but this is not the case for some of the higher states. In particular the optimum angle of the ^1A_g state is about 40° and has an energy comparable to the $^1B_{1g}$ state of the square. With this small angle of 40° this ^1A_g state corresponds roughly to a central H_2 ($R=1.74$) with an H on either side 2.39 bohr away. From these calculations it appears that if the side length is optimized it would be ∞ corresponding to an H_2 plus an H at $+\infty$ and an H at $-\infty$. Thus this state could lead to a barrier height as low as the bond energy of H_2 but would not be a transition state relevant for the four-center reaction.

In Fig. 15 and Table VI we show the lower states of 60° rhombus H_4 as a function of side length. Although ^1A_g and $^1B_{1g}$ are nearly equal in energy near $R=2.5$, at this angle the ^1A_g angle is strongly favored over $^1B_{1g}$ for smaller internuclear distances indicating a crossing of these states at larger angles.

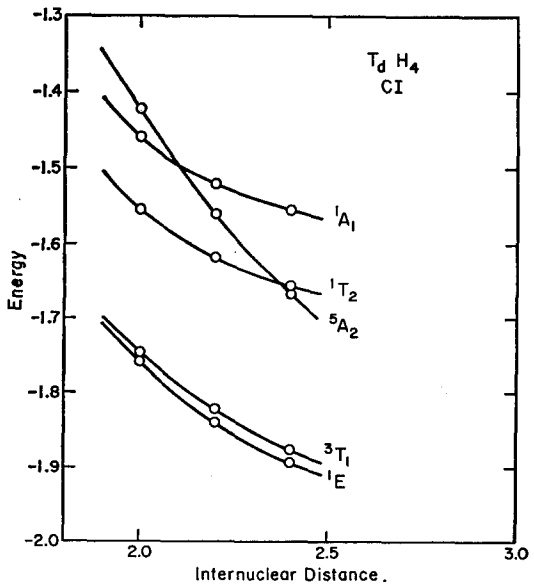


FIG. 9. The CI energy (in hartrees) of tetrahedral (T_d) H_4 as a function of internuclear distance (in bohrs).

The Regular Trapezoidal Configuration

Consider next the system in a geometry similar to the rectangular case discussed above, but let us now relax the restriction that the two bond lengths be the same. This is not unreasonable because Bauer and Ossa[1] have interpreted their data as indicating that one of the reactant molecules must be vibrationally excited. For H_2, their results correspond to a difference of a factor of more than 1.1 in the average molecular length at infinite separation. In any case, one of the normal modes of vibration of the square also leads to the symmetric trapezoid. Here we have imposed the symmetry of a regular trapezoid throughout the reaction.

At large intermolecular distance, the one-electron levels behave quite like those of the rectangular case shown in Figs. 2 and 3. The system never changes its

TABLE IV. The $^1E'$ state of centered equilateral triangular H_4 with a comparison of the energies obtained by the various methods. R is the center to vertex distance (in bohrs).[a]

R	E(CI)	E(G1)	E(HF)
1.8	−1.941179	−1.940066	−1.852694
2.0	−1.983152	−1.982708	−1.876505
2.2	−2.005586	−2.005230	−1.879574
2.4	−2.016148	−2.015880	−1.869707

[a] References 13 and 17.

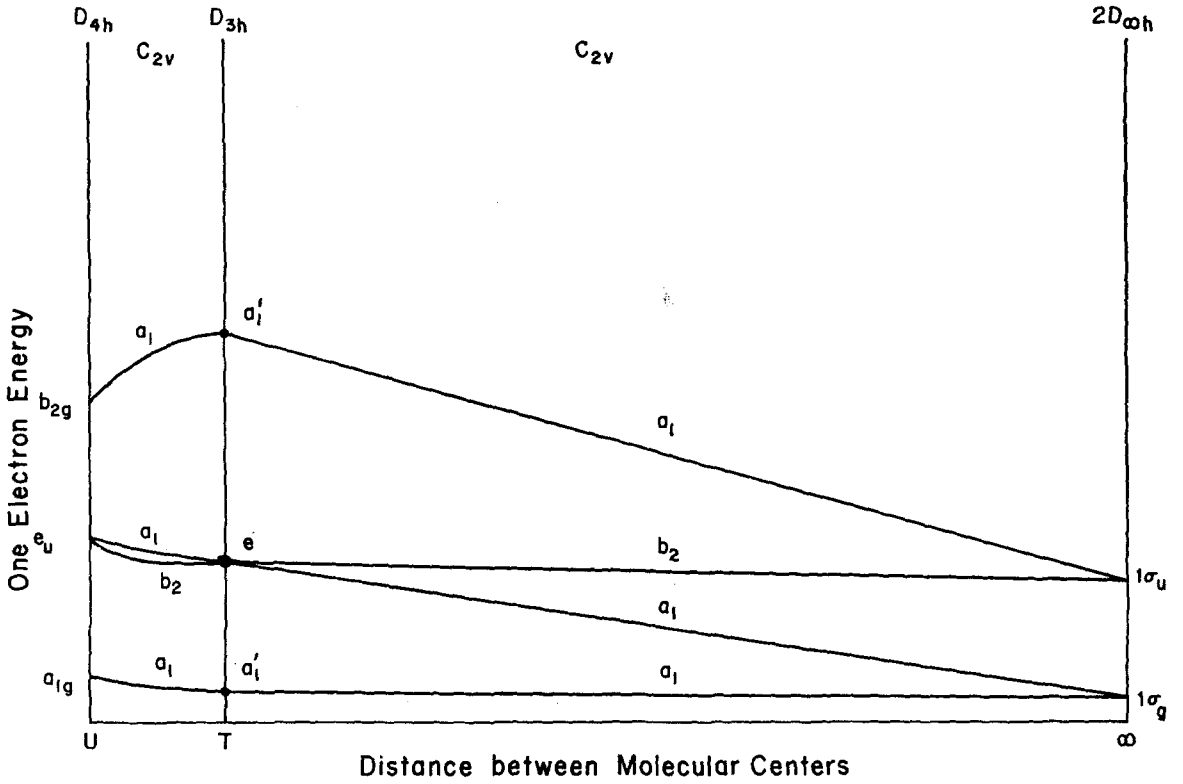


FIG. 10. The qualitative one-electron energy level scheme for perpendicular (C_{2v}) H_2+H_2, T=centered equilateral triangle, U=square (the last choice is arbitrary).

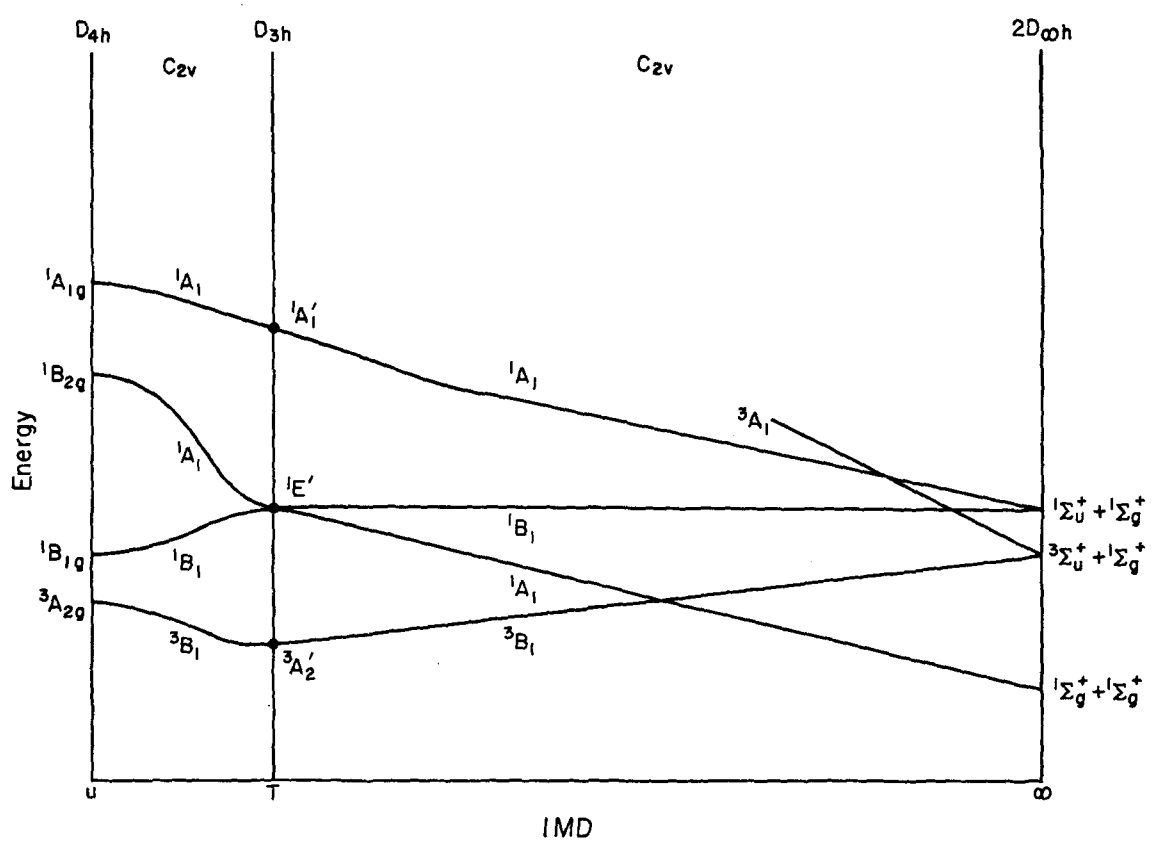


FIG. 11. The many-electron states of perpendicular (C_{2v}) H_2+H_2.

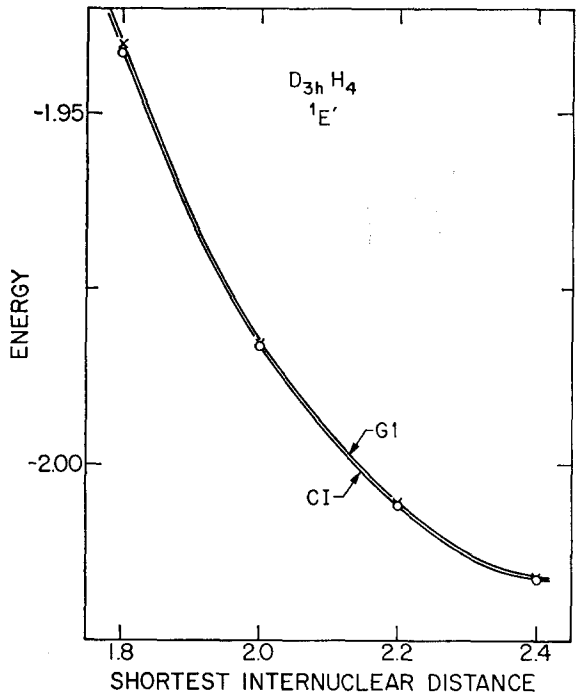


FIG. 12. The energy (in hartrees) of the $^1E'$ state of the centered equilateral triangle (D_{3h}) as a function of center to vertex distance (in bohrs) by three methods.

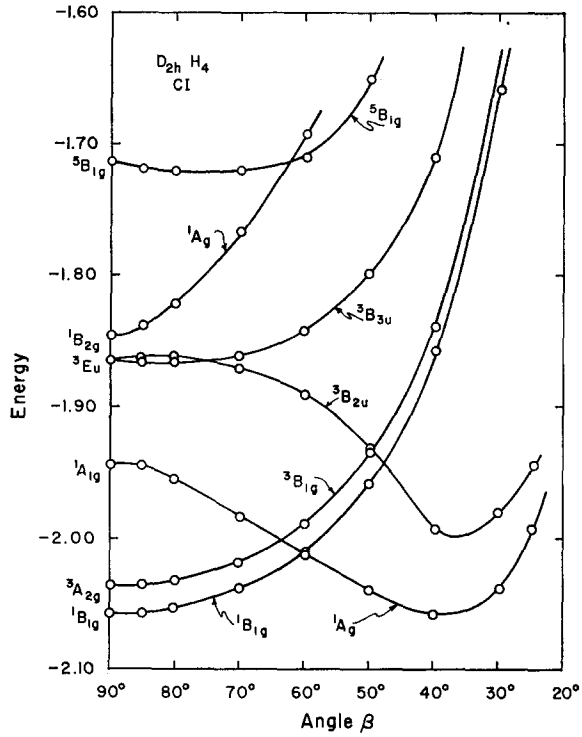


FIG. 14. The CI energy (in hartrees) of the first seven states of D_{2h} H_4 (rhombic) as a function of angle at $R=2.54$ bohr.

symmetry throughout the course of the reaction, and the degeneracies found in the square do not occur here; however, near the transition state, a crossing of the orbitals analogous to x and y obviously must occur. The transition state for the trapezoidal configuration is not metastable.

In Fig. 16 and Table VII, we show the CI reaction surface for this geometry. Because of the small number of points used to generate this surface and the errors due to basis set restrictions, Figs. 16 and 17 are meant only to give a qualitative view of the potential surface. There is a channel through which the reaction might proceed. The saddle point is encountered at a point where the intermolecular distance is approximately the average bond length of the reactant molecules, which have expanded considerably from their values at the separated molecule limit. This is the transition state of the reaction.

Near the transition state a small force keeps the

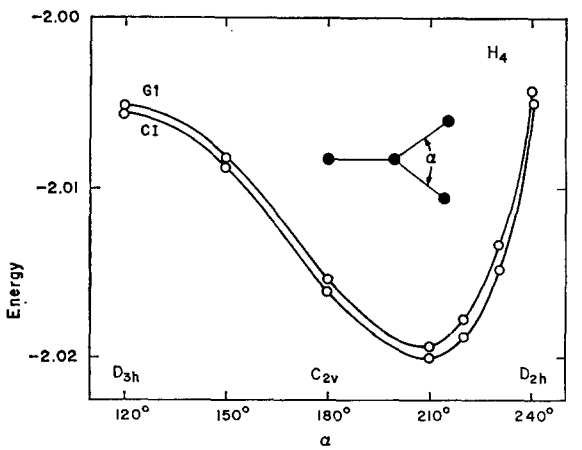


FIG. 13. The G1 and CI energies (in hartrees) for the pivotal distortion of D_{3h} H_4 to D_{2h} H_4. The three internal distances are held constant (2.20 bohr); α is as defined.

TABLE V. The energy[a] (in hartrees)[b] for the lowest singlet state as a function of interior angle for the pivotal distortion of H_4 from the centered equilateral triangle ($\alpha=120°$) to the 60° rhombus ($\alpha=240°$) configurations. The three interior distances are 2.2 bohr.

α°	E(CI)	E(G1)
120°	−2.005586	−2.005230
150°	−2.008801	−2.008194
180°	−2.016127	−2.015414
210°	−2.020078	−2.019347
220°	−2.018585	−2.017846
230°	−2.014146	−2.013350
240°	−2.004899	−2.001115

[a] Reference 13.
[b] Reference 17.
[c] See Fig. 13.

reactants from slipping parallel to one another into an irregular trapezoid. The regular trapezoid is unstable with respect to falling into the kite-shaped geometry and pseudodissociating through the trough described below.

The Kite-Shaped Configuration

As indicated above several of the above configurations are unstable with respect to distortion toward a kite shape. We carried out CI calculations for a fixed perimeter (10.16 bohr) kite and varied the angles and ratios of sides (see Fig. 17 and Table VIII). In these calculations the optimum kite configuration is one in which three of the H's are nearly linear and the other H is as far away as possible (consistent with the fixed perimeter). Thus it appears that the optimum perimeter is ∞ corresponding to linear equidistant[20] H_3 plus an H at ∞ which would be inconsistent with a four-center reaction.

The Linear Configuration

Consider the system with a large intermolecular distance (IMD) again and let $\phi_1=\phi_2=0$. In this case, the molecules are collinear, and the system has $D_{\infty h}$ symmetry. Here we have a closed-shell system throughout the approach of the two molecules. The one-electron orbitals of the system are the plus (+) and minus (−) linear combinations of the one-electron orbitals of the molecules, σ_g and σ_u, respectively. They split as expected upon shortening of the IMD, the σ_u being the higher and the gulf between them widening as IMD decreases. At all points the system remains a closed-shell system. In Fig. 18 and Table IX, we show the CI results for the case where the intermolecular distance (IMD) is twice the bond length (BL) of the two molecules, and cases where the IMD has been fixed on either side of the optimum of the above. In the same figure we have also presented the results of Griffing and Vanderslice.[21,22] Our results are at least 0.128 improved and indicate a minimum at a shorter distance. In the same figure, we also give the results for the case where the IMD is only slightly different from the optimum in the above calculations. On both sides of this point, the optimum BL's are significantly less than half of the IMD.

The energy of the $D_{\infty h}$ system stays well below that of H_2+2H over most of the reaction surface. Because there would seem to be no mechanism for the bimolecular

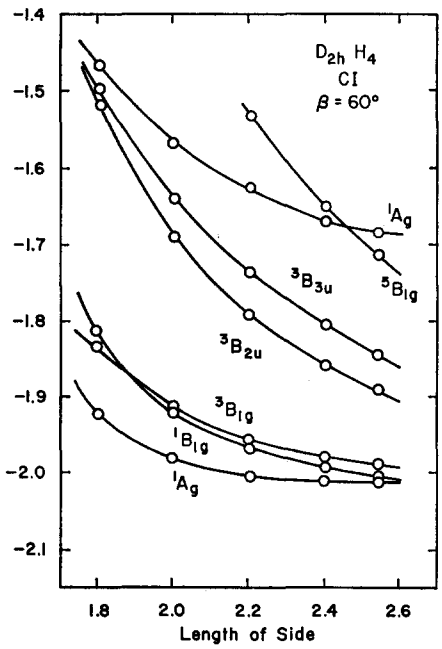


FIG. 15. The CI energy (in hartrees) of the first seven states of D_{2h} (rhombic) H_4 as a function of the length of the side (in bohrs) at $\beta=60°$.

[20] We obtain linear equidistant H_3 here rather than the lower energy H_2+H because of the restrictions to the C_{2v} symmetry of the kite.

TABLE VI. The CI energy[a] (in hartrees)[b] of the rhombus as a function of angle (β) for $R=2.54$.

β	$E(^1B_{1g})$	$E(^3B_{1g})$	$E(^1A_g)$
90°	−2.057685	−2.036984	−1.932776
85°	−2.056602	−2.035926	−1.947097
80°	−2.053275	−2.032677	−1.956754
70°	−2.038746	−2.018468	−1.983156
60°	−2.011605	−1.989877	−2.009607
50°	−1.955868	−1.936962	−2.038447
40°	−1.855936	−1.838221	−2.056376
30°	−1.658478	−1.642514	−2.038675
25°	−1.545165	−1.487226	−1.991373

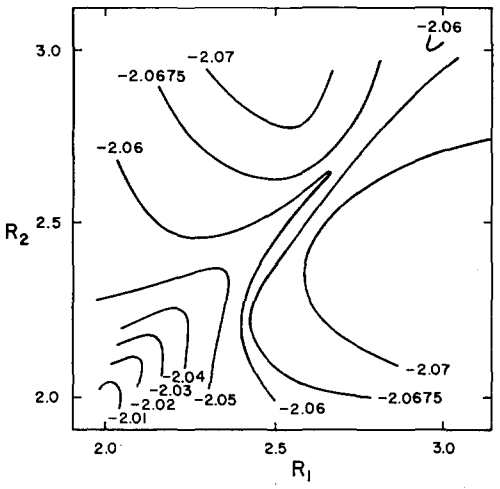
The CI energy of the rhombus as a function of length of side (R) for $\beta=60°$

R	$E(^1A_{1g})$	$E(^1B_{1g})$	$E(^3B_{1g})$
1.8	−1.923467	−1.834704	−1.822804
2.0	−1.980709	−1.920609	−1.912535
2.2	−2.004899	−1.969314	−1.955954
2.4	−2.012172	−1.997754	−1.980222
2.54	−2.011605	−2.009607	−1.989877

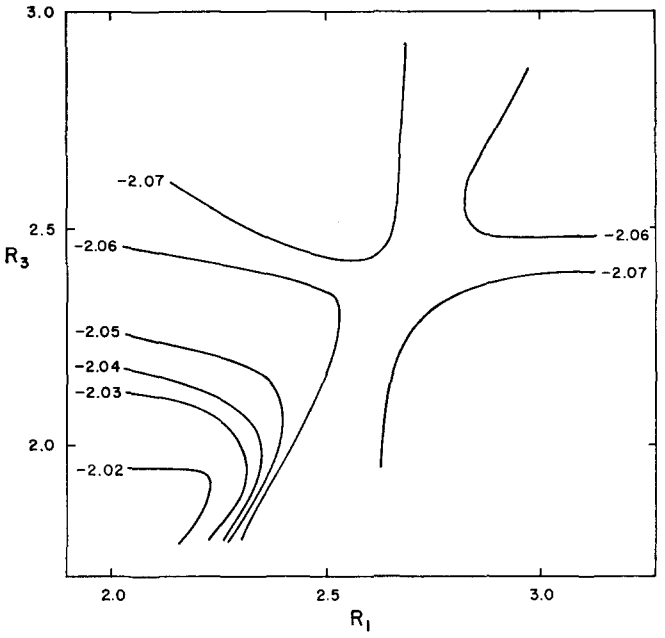
[a] Reference 13.
[b] Reference 17.

[21] V. Griffing and J. Vanderslice, J. Chem. Phys. **23**, 1035 (1955). These calculations use an orbital exponent of 1.0 (1.15 would be more appropriate), use approximate integrals, and neglect configurations.

[22] R. Taylor, Proc. Phys. Soc. (London) **64A**, 249 (1951) has done similar calculations; our results indicate a minimum at least 0.127 below the CI result cited by Taylor, but he uses too short an internuclear distance (1.4), an orbital exponent of 1.0, and neglects configurations.

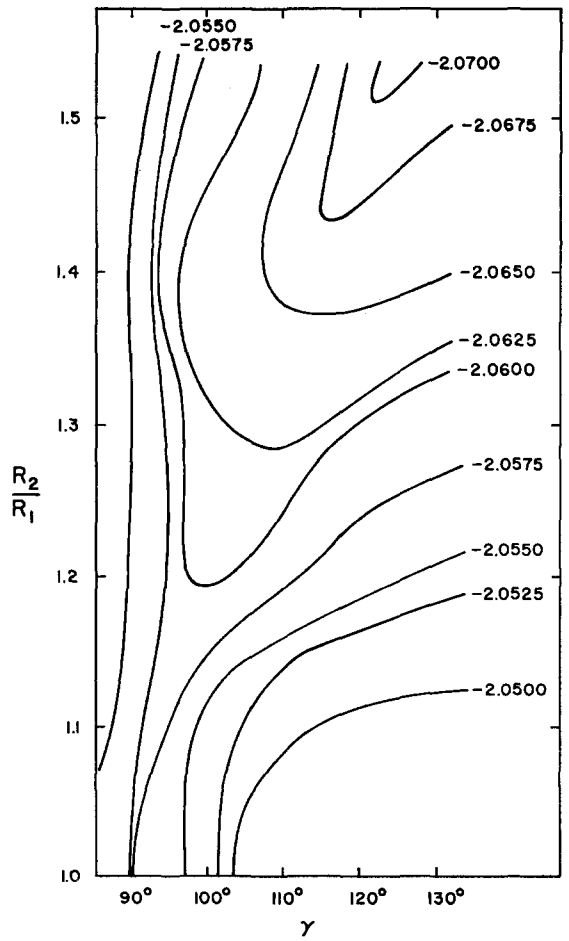


(a)

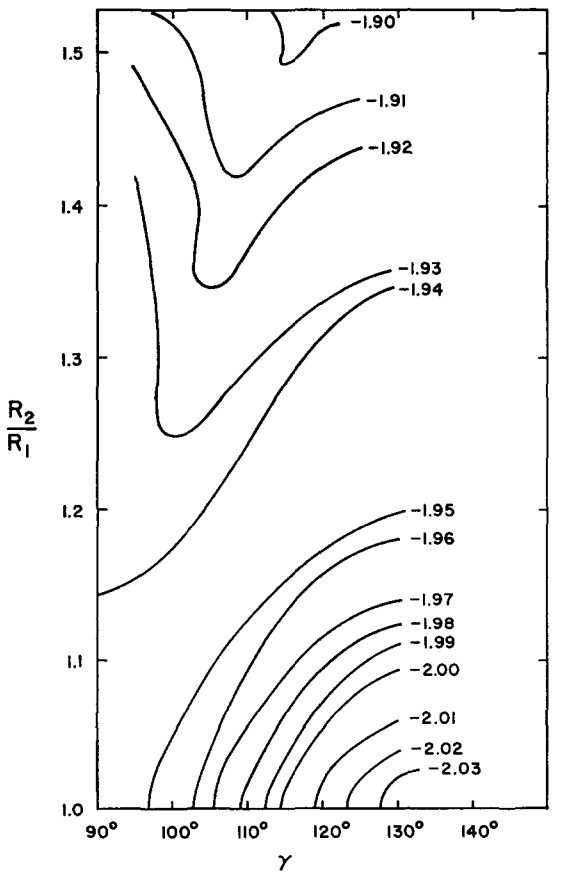


(b)

FIG. 16. (a) A portion of the CI reaction surface for the regular trapezoid; each contour is for an approximately optimum value of R_3/R_4. (b) A portion of the CI reaction surface for the regular trapezoid; each contour is for an approximately optimum value of R_2/R_4.



(a)



(b)

FIG. 17. (a) The CI reaction surface for the ground singlet state of kite-shaped H_4 ($R_1+R_2=5.08$ bohr, energies in hartrees). (b) The CI reaction surface of the second singlet state of kite-shaped H_4 [parameters as in (a)].

TABLE VII. The CI energy[a] of regular trapezoidal H_4 (in hartrees).[b]

R_1[c]	R_2[c]	R_3[c]	R_4[c]	E(CI)
2.068434	2.07	1.89	2.25	−2.013174
2.289826	2.3	2.1	2.5	−2.046035
2.5276086	2.53	2.31	2.75	−2.059076
2.7653912	2.76	2.52	3.0	−2.060689
2.2420348	1.994	1.738	2.25	−2.048817
2.471074	2.247	1.969	2.525	−2.068715
2.7	2.5	2.2	2.8	−2.072678
2.9289826	2.753	2.431	3.075	−2.067909
1.9804048	2.138483	2.035288	2.241678	−2.023849
2.2093874	2.3914298	2.266288	2.51667796	−2.056679
2.43837	2.6444829	2.497288	2.79167796	−2.067916
2.6673526	2.8974829	2.728288	3.06667796	−2.067174

[a] Reference 13. [b] Reference 17 [c] See Fig. 1.

TABLE VIII. CI energy (in hartrees)[a] of kite-shaped H_4 for a perimeter of 10.16 bohr.

R_2/R_1[b]	γ[b]	E
1.0	90°	−2.057685
	95°	−2.056602
	100°	−2.053275
	110°	−2.038746
1.1	90°	−2.057373
	100°	−2.057949
	110°	−2.051286
1.2	90°	−2.056215
	100°	−2.060688
	110°	−2.058750
1.3	90°	−2.054960
	100°	−2.062029
	110°	−2.063421
	120°	−2.059841
1.4	100°	−2.061952
	110°	−2.065965
	120°	−2.065456
1.5	100°	−2.060374
	110°	−2.066593
	120°	−2.068458

[a] References 13 and 17.
[b] See Fig. 1.

interchange of nuclei which would proceed at an appreciable rate here, this is simply an unreactive collision of the two molecules. In large systems, this might also be a significant point on the regular trapezoidal reaction path.[23] Thus the linear configuration which was so valuable in the free radical process[7,24,25] is of little interest for the four-center exchange reaction.

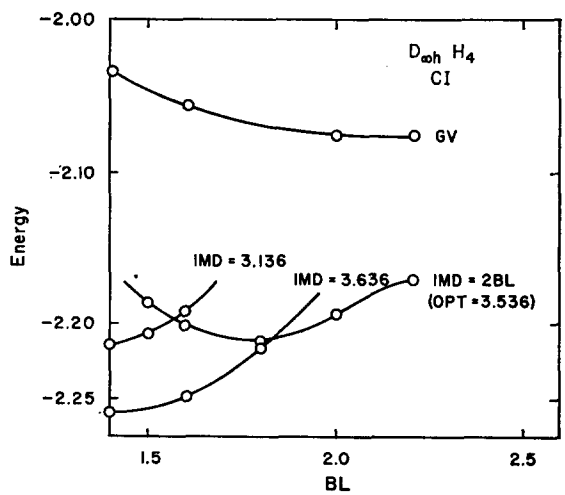


FIG. 18. The CI energy (in hartrees) of $D_{\infty h}$ H_4. GV indicates the Griffing-Vanderslice (Ref. 21) results for IMD = 2 BL.

[23] The Eyring [Los Alamos Scientific Laboratory Colloquium, (Los Alamos, N.M., Oct. 1964) and 1967 Southwest Regional A.C.S. Meeting (Little Rock, Ark., Dec. 1967); see also R. M. Noyes, J. Chem. Phys. **48**, 323 (1968)] linear transition state for the

$$H_2 + I_2 = 2HI$$

reaction could also be achieved through the regular trapezoidal approach, thus his argument is rendered somewhat less conclusive.

[24] I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, J. Chem. Phys. **48**, 2700 (1968).

[25] M. Karplus, R. N. Porter, and R. D. Sharma, J. Chem. Phys. **43**, 3259 (1965).

TABLE IX. CI energy[a] (in hartrees)[b] of linear H_4.

IMD[c]	BL[c]	E
4.4	2.2	−2.172172
4.0	2.0	−2.192681
3.6	1.8	−2.210793
3.2	1.6	−2.201130
3.0	1.5	−2.182065
3.636	1.8	−2.214060
	1.6	−2.246961
	1.4	−2.258413
3.136	1.6	−2.190464
	1.5	−2.206438
	1.4	−2.214456
4.5	1.5	−2.284743
4.0	1.4166	−2.279274
5.0		−2.293049
6.0		−2.295379
7.0		−2.295740
8.0		−2.295791
∞	1.4166	−2.295810

[a] Approximately optimized orbital exponents used in this calculation.
[b] Reference 17.
[c] See Fig. 1.

A number of points were examined in the region of the experimental van der Waals minimum[26] (see Table IX) but no evidence of such a minimum has been located. This is probably due to the limitation of our calculation to σ-type functions. Such a minimum arises from dynamic correlation such as is afforded by π (and higher)-type functions. This will be discussed in greater detail in a later work.[27]

THE BARRIER HEIGHT

The lowest energies calculated for the possible transition states of the square and symmetric trapezoid configurations were −2.060 and −2.061, respectively, whereas the calculated energies for possible transitional states with centered equilateral triangular and tetrahedral configurations were much higher. For the ^1A_g rhombus and symmetric trapezoid configurations the lowest energies probably correspond to those of H_2+2H and H_3+H, respectively; however, these configurations should not be important for the four-center reaction. Using −2.06 for the transition state energy, the predicted barrier height (using −2.2958 for the energy of two H_2 molecules) is 0.236 (148 kcal/mole). Similar calculations for H_3 (minimum basis set CI) yielded a barrier height about 0.025 (16 kcal/mole) higher than that calculated using large basis sets. We would expect a similar error for H_4[28] and thus a barrier of 0.211 (132 kcal/mole). This is to be compared to measured activation energies of 0.068 (42 kcal/mole) according to Bauer and Ossa[1] and 0.064 (40 kcal/mole) according to Burcat and Lifshitz.[1] One source of error in the barrier height is the use of a minimum basis set. The resulting error in the energy is about 0.025 (16 kcal/mole) for H_4; this error should be rather independent of the geometry near the transition state and should not account for the difference in the calculated and experimental energy. Considering the sources of error we would expect the barrier for the four-center exchange reactions to be within 20 kcal/mole of the predicted 132 kcal/mole. Recently completed larger basis set calculations all fall within this range.[29–31]

Allowing the reacting molecules to pass through the region of the square as shown in Figs. 5 and 13–17, which is very flat and unbound along four of the six normal modes, we may expect the transition state to have a low vibrational energy (e.g., 0.0037 hartrees for the square of side 2.54 bohr). Thus we may reasonably expect most of the vibrational energy, both preexcitation and zero point, to be effectively added to the separated molecule limit. Taking a probable error of 0.025 into account, we find a barrier height of 0.211 (132 kcal/mole) neglecting preexcitation, and using the Bauer and Ossa value for the preexcitation, a height of 0.162 (101 kcal/mole). Even including this vibrational preexcitation, the predicted barrier height is at least a factor of two higher than the experimental activation energy.

In the region of the transition state, the lowest state of centered equilateral triangular H_4 is the triplet state, $^3A_2'$ (minimum energy, −2.0753 at $R=2.334$). Thus if the spin–orbit interactions are sufficient to allow the incoming singlet H_2+H_2 to cross to the triplet state, we would obtain a decrease in the effective potential barrier. Inclusion of spin–orbit coupling allows the $^1A_1$ state to connect with one component of the $^3B_2$ state. However, this would decrease the barrier height by only 0.015 (9 kcal/mole) and thus would not account for the difference between the theoretical and experimental barriers. In addition we would not expect the spin–orbit

[26] R. G. Gordon and J. K. Cashion, J. Chem. Phys. **44**, 1190 (1966).
[27] C. W. Wilson, Jr., and W. A. Goddard III (unpublished).

[28] Using 23.4 kcal/mole for the predicted barrier of H_3 for an optimized minimum basis set CI calculation (Ref. 24) and an experimentally obtained value of 8.5 kcal/mole [R. E. Weston, Sr., J. Chem. Phys. **31**, 892 (1959)], we obtain an error of 14.9 kcal/mole or 0.025 hartree. Since the H_4 calculations published here are for approximately optimized orbital exponents and since the distances are larger in H_4 than in H_3, we would expect a comparable error in the barrier height from our calculations.
[29] R. M. Stevens (private communication).
[30] L. Pedersen (private communication).
[31] *Note added in proof:* M. Rubinstein and I. Shavitt (to be published) have reached similar conclusions.

interactions in H_4 to be sufficient to lead to a significant number of such transitions.

DISCUSSION

We have considered most of the reasonable geometries for the bimolecular exchange reaction of H_2+D_2. In all cases the resulting transition states are at an energy significantly higher than the energy of H_2+2H. However the activation energy from the shock-tube experiments is less than half the energy required to break the H_2 bond. We believe that the most likely nuclear configurations for a four-center exchange reaction have been considered and that an increase in the basis set would not decrease the theoretical energies for the four-center transition state below the H_2+2H energy. If this is the case then the theoretical and experimental results are consistent only if the exchange reaction in the shock tube is *not* through a four-center bimolecular mechanism. We have assumed here that the activation energy would be close to the calculated barrier height. In order to determine the actual difference between these quantities, it is necessary to carry out trajectory calculations of the type pursued by Karplus, Porter, and Sharma[25] on the H_3 system and those of Raff[32] on $K+C_2H_5I$. Trajectory calculations for H_2+H led to an activation energy 0.003 lower than the barrier height, and calculations on a similar surface for H_2+H_2 indicate a similar decrease.[30]

One of the purposes of these calculations was to obtain information concerning the transitions states and changes in bonds for the H_2+D_2 four-center bimolecular reaction which might be applied to larger systems that are presently too large for *ab initio* calculations. Since our calculations indicate that the exchange reaction does not proceed through this mechanism for H_2+D_2, it is not clear how relevant our conclusions can be for discussing systems that do exchange via this mechanism. We found that planar states are more favorable than nonplanar states (with the tetrahedron quite unfavorable) and that linear states are most favorable. Thus for systems[33] A_2+B_2 in which the B_2 bond is much weaker than the A_2 bond as in H_2+I_2 or in which A_2B is stable, the linear configurations may be the transition state if B atoms are available. We found the square configuration to be favorable for some states whereas others definitely favored a quite distorted rhombic configuration. However the latter effect was primarily due to the energy of H_4 being much greater than that of H_2+2H and need not occur if the opposite were true. It is less clear how to compare the square and centered-equilateral-triangular (CET) configurations for other systems, although the CET might be favored by the weakly bound molecules involving bonds with primarily s character, such as the Na_2+Na_2 case.[33] In addition one would expect the CET to be favored for the $D_2+H_2^+$-type exchange. Discussions of the changes in bond orbitals will be reserved for a separate paper.

[32] L. M. Raff, J. Chem. Phys. **44**, 1201 (1966).
[33] R. M. Noyes, J. Am. Chem. Soc. **88**, 4311, 4318, 4324 (1966).

CONCLUSIONS

A systematic search of the six-dimensional potential "surface" in the region where one might expect to locate the transition state for the bimolecular four-center exchange reaction has been carried out by two different quantum-mechanical techniques within the adiabatic approximation, but has failed to locate a point with an energy below that of H_2+2H.

The optimum tetrahedral, square, rhombic, centered-equilateral-triangular, and trapezoidal configurations were considered; all led to too high an energy and none led to a metastable transition state. These calculations indicate a barrier height about three times the experimental activation energy from the shock-tube experiments.

It should be emphasized here that our conclusions concerning the nature of the mechanism of this reaction refer specifically to *this* reaction, not to the four-center exchange reaction in general. The ideas presented herein should be considered in a discussion of other four-center exchange reactions, but may not be applicable where there are additional internal coordinates available to absorb and release energy.

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